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Experimental Determination of the Elastic Moduli of Polymer Crystals in the Direction Perpendicular to the Chain Axis

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Experiments were carried out to prove the validity of the assumption for the calculation of the elastic modulus of polymer crystals from X-ray determination of lattice extension, that, in the direction perpendicular to the polymer chain axis, the stress is homogeneous. Films with various draw-ratios and heat treatments were prepared from polyvinyl alcohol; the elastic moduli of crystalline regions of these films calculated on the above assumption were only slightly different from one another. This fact may be regarded as a strong support for the assumption. The slight difference was attributed to small changes of the lattice spacing. Similar experiments were also carried out for polyethylene.

INTRODUCTION

In some previous papers, we have determined by an X-ray method the elastic moduli of various high polymer crystals in the directions parallel¹⁾ and perpendicular^{2,3)} to the chain axis. In order to calculate the elastic modulus of crystalline regions, it is necessary to know the values of the stress on the crystalline regions and the extension of the crystal lattices. The extension of the crystal lattices can be measured with a high accuracy by an X-ray diffractometer, whereas it is impossible at present to measure directly the stress on the crystalline regions. Therefore, the elastic modulus was calculated on the assumption that the stress was homogeneous throughout the length and breadth of the specimen; that is, it was assumed that the stress on the specimen was equal to that on the crystalline regions. In the case of the elastic moduli of the polymer crystals in the chain-axial direction, the validity of this assumption was proved to be correct within the experimental errors⁴⁾. However, it is not as yet verified experimentally for the elastic moduli in the direction perpendicular to the chain axis.

In the present study we have tried to ascertain experimentally whether the above assumption for the elastic moduli perpendicular to the chain axis is correct or not. That is, experiments are carried out for the specimens with widely different degrees of orientation of crystallites or crystallinity, and if the elastic moduli calculated on the above assumption agree with each other within experimental error, it may be considered that the above assumption is correct.

First, experiments were carried out using polyvinyl alcohol (PVA) films, degree of crystallinity of which could be easily changed to a large extent. The measurements of the elastic moduli perpendicular to the chain axis were made for films

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with various degrees of orientation and crystallinity, which were prepared by changing draw-ratio and temperature of heat-treatment.

Special attention has been paid to an important fact that the equatorial lattice spacings of specimens vary with changing draw-ratio and heat-treatment, as will be shown later.

Second, the experiments for polyethylene (PE) films were also carried out. Polyethylenes, high and low densities, give easily films with different crystallinities. It is interesting to compare the elastic moduli of these samples in connection with the examination of the assumption described above. It is also to be noted that lateral spacings change with branching, as is well-known^{6,11}. The similar experiments have also been performed for γ -ray irradiated polyethylenes, because it seemed to be interesting to know the effect of crosslinking produced in the crystal lattices on the elastic modulus of crystalline regions.

EXPERIMENTAL

1. Samples

PVA films. The raw films were prepared from PVA powder of Kurashiki Rayon Co. in the following manner. The powder was washed several times with deionised water and dissolved in hot water, and a solution of 7% was prepared, which was poured on a glass plate on mercury and dried up at room temperature. By drawing these raw films in a silicon oil bath at 100°C and annealing at fixed length for 3 min. at 210°C, films with various draw-ratios were produced. Then these films were thoroughly washed in benzene and dried for an hour at 90°C. In the case of films with various heat treatments, water-swollen raw films were 300% stretched and subjected to heat treatment at fixed length at each temperature after drying. The relevant data for PVA samples are listed in Tables 1 and 2. Figures 1 and 2 show their X-ray diagrams. Orientation is almost complete for

Table 1. Effect of Draw-Ratio on Properties of PVA Films.

Draw-ratio	Thickness (mm)	Density (g./cm.)	Degree of crystallinity	Degree of orientation H
1	0.12	1.302	0.45	0
1.3	0.16	1.303	0.46	—
1.5	0.15	1.305	0.49	0.86
3	0.40	1.307	0.51	0.95
6	0.40	1.307	0.51	0.96
11	0.35	1.304	0.47	0.97

Table 2. Effect of Temperature of Heat Treatment on Properties of PVA Films.

Temperature (°C)	Thickness (mm)	Density (g./cm ³)	Degree of crystallinity	Degree of orientation H
25	0.15	1.290	0.29	0.90
100	0.15	1.302	0.45	0.93
160	0.13	1.309	0.54	0.95
200	0.16	1.311	0.57	0.96

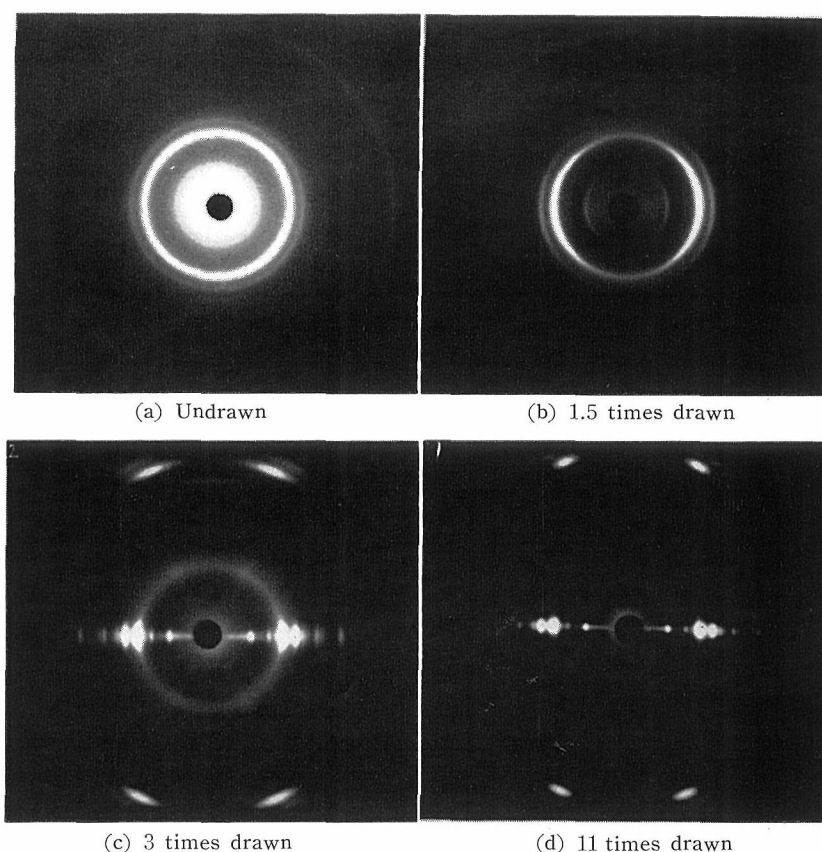


Fig. 1 X-ray diagrams of drawn PVA films

X-ray beam is perpendicular both to chain axis and to film surface. Camera distance : ca. 4cm

draw-ratio of 2 or 3 as is shown in Fig. 1. The higher the temperature of the heat treatment, the clearer the X-ray patterns (see Fig. 2). It means that the crystallinity increases with rising temperature.

PE films. Polyethylene samples used are a high density linear polyethylene of Scholex 6050 (a commercial product which corresponds to Marlex 50) and low density branched polyethylenes, Sumikathene F101-1 (M.I.=0.3) and Sumikathene G 806 (M.I.=50). The oriented films of Scholex 6050 were prepared by drawing films prepared by a melt pressing method at 90°C. The γ -ray irradiated films were prepared by cold-drawing at room temperature. All of these films were 1200% stretched and annealed at fixed length for two hours at 100°C. Sumikathene F101-1 was 400% stretched at 90°C and annealed at fixed length for two hours at 110°C. Similarly Sumikathene G806 was stretched 400% at room temperature and annealed at fixed length for two hours at 80°C. γ -Ray irradiation was performed with Co⁶⁰ (dose rate; 7.05×10^4 r/hr.) at 10^{-3} mmHg. The total dose was 3.1×10^7 r.

The relevant data for PE samples are listed in Table 3. X-ray diffraction patterns of these samples are shown in Fig. 3. X-ray patterns of the irradiated samples are not given here, since they are virtually the same as those of the unirradiated samples. Fig. 3a shows that Scholex 6050 sample has a double orientation ((110) and (100) planes are parallel to the film surface).

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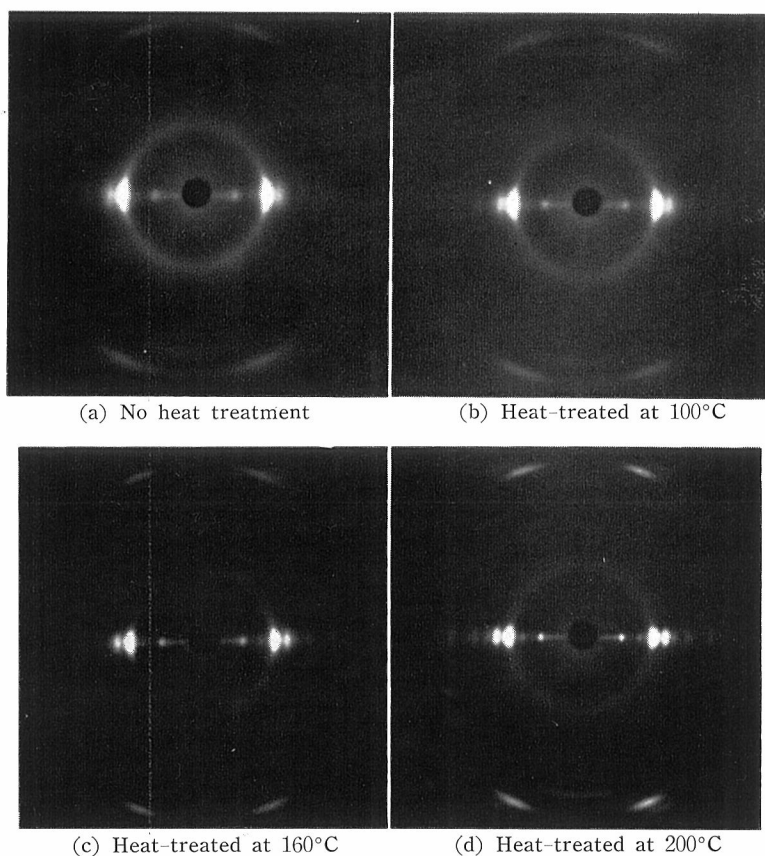


Fig. 2 X-ray diagrams of heat treated PVA films
X-ray beam is perpendicular both to chain axis and to film surface. Camera distance : ca. 4cm

Table 3. Some Properties of Various Polyethylene Films.

Sample	Thickness (mm)	Density (g./cm ³)	Degree of crystallinity	Degree of orientation <i>H</i>	Degree of branching (CH ₃ /1000C)	Gel product (%)
Unirradiated						
Scholex 6050	0.04	0.962	0.80	0.975	~0	
Hizex 5000*	0.1	0.945	0.72	0.972	0~3	
Sumikathene F101-1	0.21	0.924	0.59	0.961	~10	
Sumikathene G806	0.14	0.916	0.54	0.961	~20	
γ -Ray irradiated						
Scholex 6050**	0.05	0.933	0.66	0.979		68.8
Sumikathene F101-1	0.22	0.924	0.59	0.956		77.7
Sumikathene G806	0.23	0.916	0.54	0.957		59.1

*) Reported previously.

**) Milk-white film (considered to contain much void).

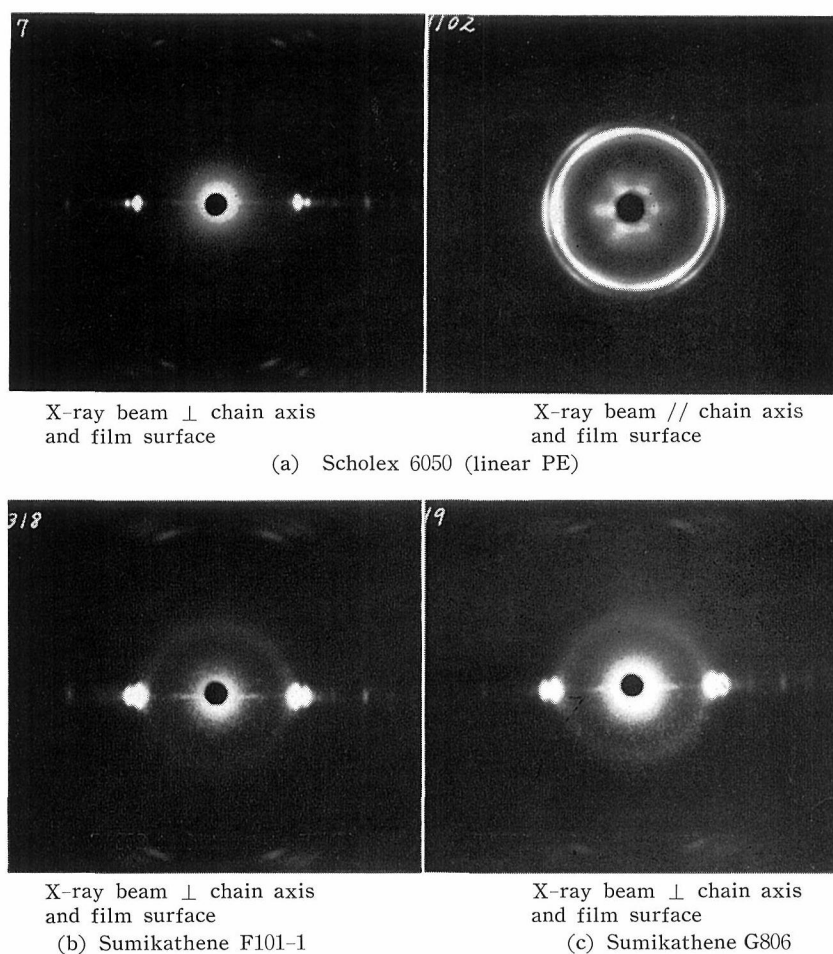


Fig. 3 x-ray diagrams of polyethylene films.
Camera distance : ca. 4cm

2. Measurements

Elastic Modulus. Measurements of elastic moduli of crystals and specimens were carried out following the method described in the previous paper²⁾. Crystal net planes employed are (101) and (110) for PVA and PE, respectively. Diffraction angles of these lattice planes are $2\theta = 19^\circ 20' \sim 24'$ and $21^\circ 26' \sim 36'$. The lattice extensions corresponding to $\Delta 2\theta$ (the amount of movement of $2\theta = 1'$) are 0.085% and 0.077%. As an elongation of the specimen, the value at 60 seconds after loading was employed. Measurements were made at $20 \pm 1^\circ\text{C}$, and at an RH of $60 \pm 5\%$ for PVA and at $25 \pm 2^\circ\text{C}$, and $55 \pm 5\%$ for PE except for the irradiated polyethylene sample at $20 \pm 1^\circ\text{C}$, and $60 \pm 5\%$.

Lattice Spacing. Aluminium powder was used to standardize lattice spacings. The reference is the (111) plane. A diffractometer was used in the measurement. The experimental error is $\pm 1'$ in 2θ . Measurements were carried out at $20 \pm 1^\circ\text{C}$ on the same condition.

Density. Densities were measured at $30 \pm 0.1^\circ\text{C}$ in benzene-carbon tetrachloride

and ethanol-water system for PVA and PE, respectively.

Degree of Crystallinity. Degrees of crystallinity were calculated from densities measured above with the following values for densities of crystalline and amorphous regions (ρ_c and ρ_a).

PVA⁶⁾ $\rho_c=1.345$ $\rho_a=1.269$

PE⁷⁾ $\rho_c=1.007$ $\rho_a=0.815$

Degree of Orientation. The practical standard of orientation H° was used to express the relative change in orientation of crystallites.

$$H = (180^\circ - H^\circ)/180^\circ,$$

where H° is the half-value of an inclined angle-density curve for the meridional reflection (020 and 002 for PVA and PE, respectively.)

Degree of Branching. There have been reported in many papers⁵⁾ on the study concerning the relationship between lattice spacing and degree of branching for polyethylene. It is known that the lateral spacings increase with increasing degree of branching. Therefore, the degrees of branching for polyethylene samples can be estimated using this relation. In this experiment they were obtained from (110) and (200) planes of undrawn samples.

Amount of Gelation. γ -Ray irradiated polyethylene samples were immersed in hot *p*-xylene for about 10 hours at 120°C and 80°C for Scholex 6050 and other polyethylenes, respectively. The films then were dried up and weighted.

EXPERIMENTAL RESULTS AND DISCUSSION

PVA The effect of draw-ratio on density is shown in Fig. 4. The density increases at first with increasing draw-ratio, and then begins to decrease at a draw-ratio of 4~5. As shown in Fig. 5, the density also increases as the temperature of heat treatment is raised.

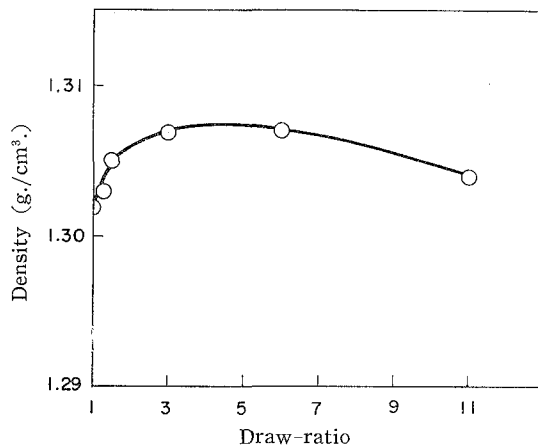


Fig. 4 Draw-ratio dependence of density of PVA film.

The relation between draw-ratio and degree of orientation is shown in Fig. 6, from which it is seen that the degree of orientation of crystallites levels off at a draw-ratio of 2~3. This is also clear in the X-ray diffraction patterns of Fig. 1.

The stress-strain (σ_t - ϵ) curves of the (10 $\bar{1}$) plane of PVA samples with var-

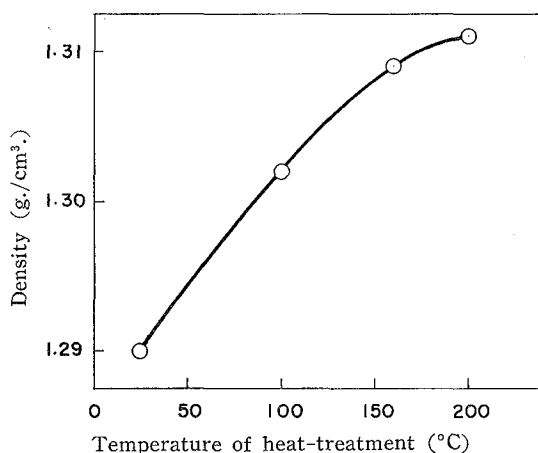


Fig. 5 Effect of temperature of heat-treatment of PVA film on density.

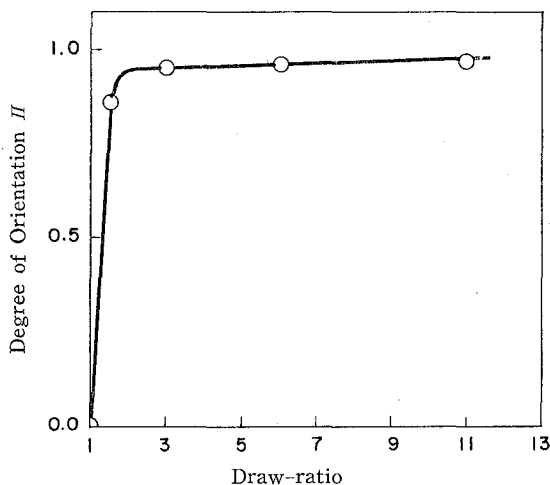


Fig. 6 Effect of draw-ratio of PVA film on degree of orientation II.

ious draw-ratios and heat treatments are given in Figs. 7 and 8. A representative line is shown in each figure. The deviation of the observed points from this line is found to be within the experimental error $\varepsilon = \pm 0.085\%$. The stress was plotted against strain separately for each draw-ratio or heat treatment, and elastic modulus of crystalline regions or specimens was evaluated from the plot. Elastic moduli (E_t and Y_t) obtained are listed in Tables 4 and 5. These plots are shown in Figs. 9 and 10. The elastic modulus tends to decrease somewhat with draw-ratio and increase with temperature of heat treatment. These changes shown in Figs. 9 and 10 seem to have a clear meaning because both of them are systematic, although they are within the range of experimental error (10% of each value). As was described above, the degree of orientation of crystallites levels off at a draw-ratio of 2~3. Nevertheless, the E_t -value continues to decrease even when the draw-ratio is above 3. Therefore, the elastic modulus does not directly depend on the degree of orientation. In addition, Sakurada and Fuchino⁹⁾ showed that the PVA film obtained from aqueous solution gave a crystalline X-ray diffraction pattern, which

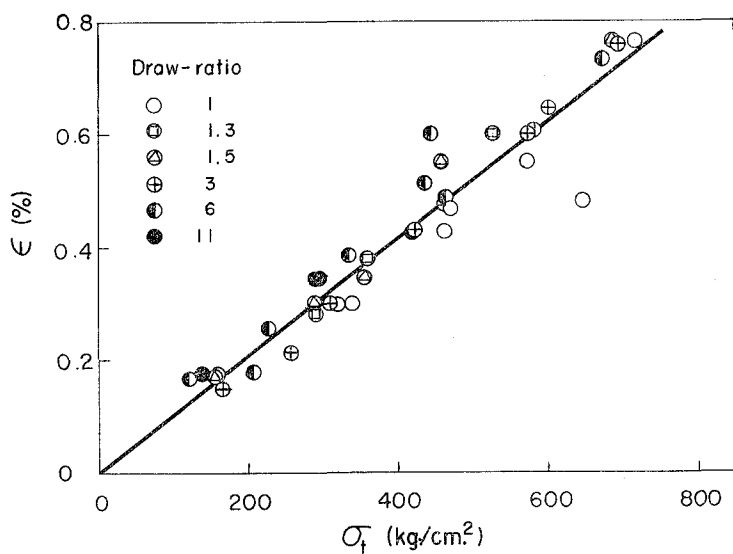


Fig. 7 Stress-strain curve for PVA lattice ($10\bar{I}$) (effect of draw-ratio).

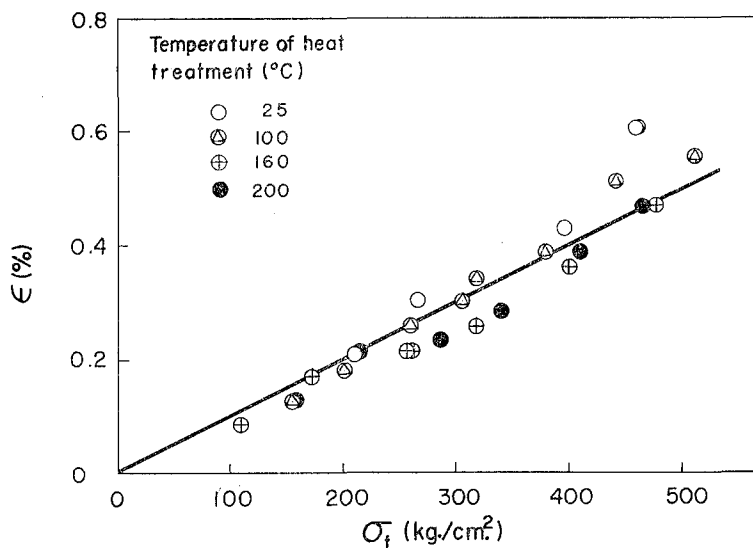


Fig. 8 Stress-strain curve for PVA lattice ($10\bar{I}$) (effect of temperature of heat treatment).

Table 4. Effect of Draw-Ratio on Elastic Moduli of PVA Films.

Draw-ratio	Lattice modulus $E_t(10\bar{I})(\times 10^4 \text{ kg./cm.}^2)$	Specimen modulus $Y_t(\times 10^4 \text{ kg./cm.}^2)$
1	10.8	7.0
1.3	9.8	5.8
1.5	9.9	7.0
3	9.8	4.7
6	9.2	5.7
11	8.5	4.0

Table 5. Effect of Temperature of Heat Treatment on Elastic Moduli of PVA Films.

Temp. of heat treatment (°C)	Lattice modulus $E_t(10\bar{1}) (\times 10^4 \text{ kg./cm.}^2)$	Specimen modulus $Y_t (\times 10^4 \text{ kg./cm.}^2)$
25	9.2	5.4
100	9.8	5.7
160	10.9	5.9
200	11.0	6.0

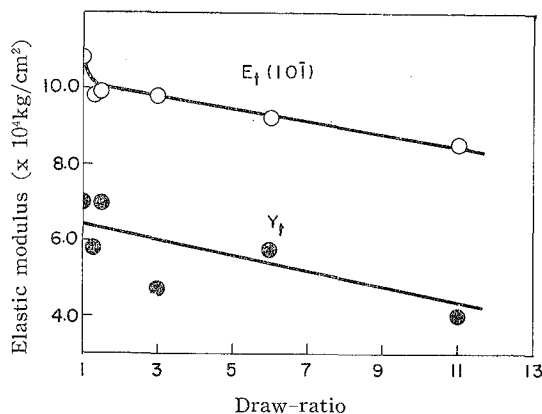


Fig. 9 Elastic modulus of lattice and specimen versus draw-ratio for PVA.

○ lattice modulus $E_t(10\bar{1})$ ● specimen modulus Y_t

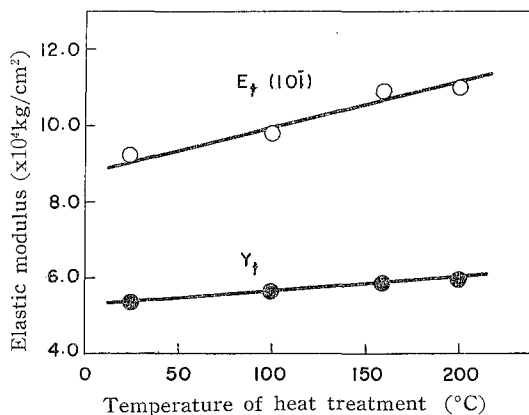


Fig. 10 Elastic modulus of lattice and specimen versus temperature of heat treatment for PVA.

○ lattice modulus $E_t(10\bar{1})$ ● specimen modulus Y_t

became remarkably sharper with heat treatment, and that some of equatorial spacings were somewhat shortened. The heat treatment thus increases the degree of crystallinity and makes the crystal structure more compact. Judging from these facts, we deduced that the small change of the elastic modulus of crystalline regions was due to the small change of lattice spacings. Then the lattice spacings of the samples were measured. The results are shown in Tables 6 and 7. The lattice spacings in the direction perpendicular to the chain axis are somewhat enlarged

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Table 6. Draw-Ratio and Lattice Spacing of PVA Film at $20 \pm 1^\circ\text{C}$.

Draw-ratio	Lattice spacing (Å)	
	(101)	(200)
1	4.579	3.909
1.3	4.587	3.911
1.5	4.583	3.914
3	4.590	3.917
6	4.587	3.919
11	4.590	3.924

Table 7. Temperature of Heat Treatment and Lattice Spacing of PVA Film at $20 \pm 1^\circ\text{C}$.

Temperature of heat treatment ($^\circ\text{C}$)	Lattice spacing (Å)	
	(101)	(200)
25	4.583	3.943
100	4.583	3.937
160	4.575	3.914
200	4.577	3.917

with increasing draw-ratio, but contract with rising temperature of heat treatment, as is shown in Figs. 11 and 12. It seems that these changes of spacings correspond to those of E_r -values shown in Figs. 9 and 10. Then the E_r -values of the (101) plane were replotted against the spacings of (101) in Fig. 13. The observed points fall on a straight line, which shows that the elastic modulus of crystalline regions is independent of the degree of orientation of crystallites and the crystallinity, but it depends only on the lattice spacing.

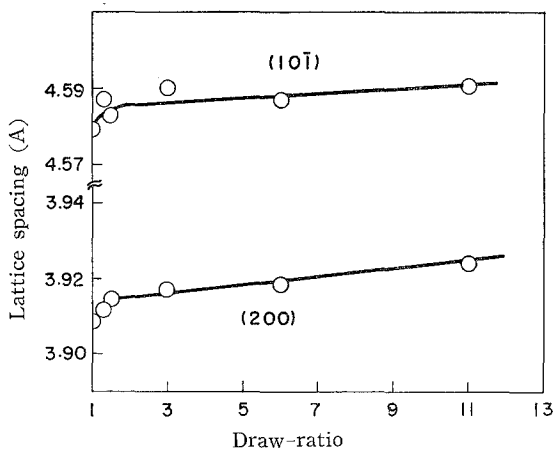


Fig. 11 Effect of draw-ratio of PVA film on lattice spacing.

PE The lattice spacings of various polyethylene samples used in the measurements are listed in Table 8. The lattice spacings are considerably different between Scholex 6050 and Sumikathene G806. This difference is large enough compared to the experimental error, since the difference of the (110) spacing be-

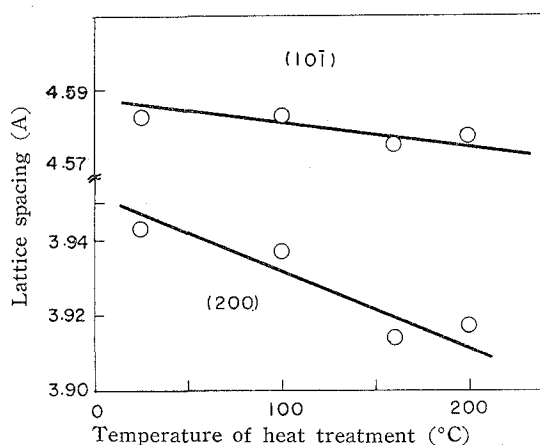


Fig. 12 Effect of temperature of heat treatment of PVA film on lattice spacing.

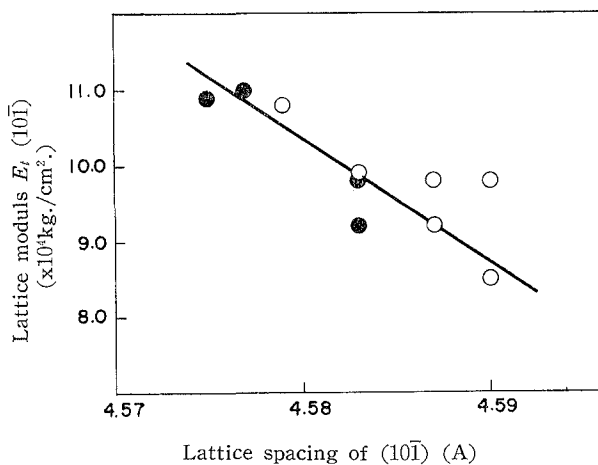


Fig. 13 Relation between lattice spacing and elastic modulus for (110) of PVA.

○ specimen with different draw-ratio,
● specimen with different temperature of heat treatment.

Table 8. Lattice Spacings of Various PE Drawn Films at $20 \pm 1^\circ\text{C}$.

Sample	(110)	Lattice spacing (Å)	
		(200)	(020)
Unirradiated			
Scholex 6050	4.114(4.114)	3.722	2.461
Hizex 5000	4.123(4.120)	3.728	2.467
Sumikathene F101-1	4.142(4.139)	3.752	2.471
Sumikathene G806	4.158(4.149)	3.759	2.475
γ -Ray irradiated			
Scholex 6050	4.115	3.728	2.465
Sumikathene F101-1	4.147	3.760	2.474
Sumikathene G806	4.154	3.759	2.478

Cf. Numbers in parentheses are the values for undrawn samples.

tween them is more than 1%, whereas the error is $\pm 0.08\%$. The spacings tend to be enlarged by drawing and γ -ray irradiation, but the amount of change is very small and is within the experimental error. Hence the degree of crosslinking in the crystalline regions seems to be small.

The stress-strain curves of the (110) planes and specimens for these samples are given in Figs. 14, 15, and 16. The curve for Hizex 5000 is not given here because it was previously reported²⁾. In all cases, straight lines passing through the origin are obtained. The E_t and Y_t values obtained from the slopes of these lines

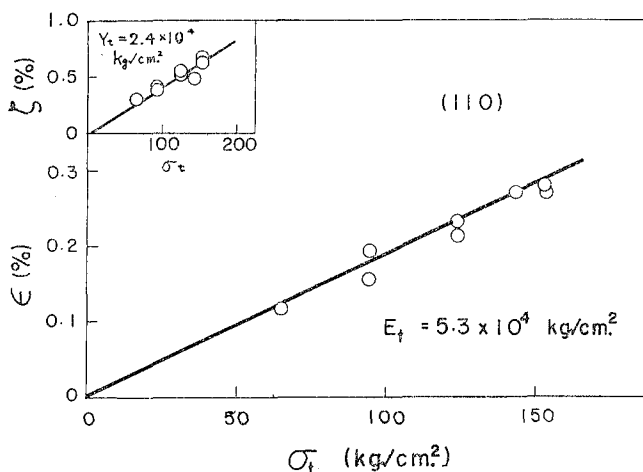


Fig. 14 Stress-strain curves for the lattice and the specimen of high density PE (Scholex 6050).

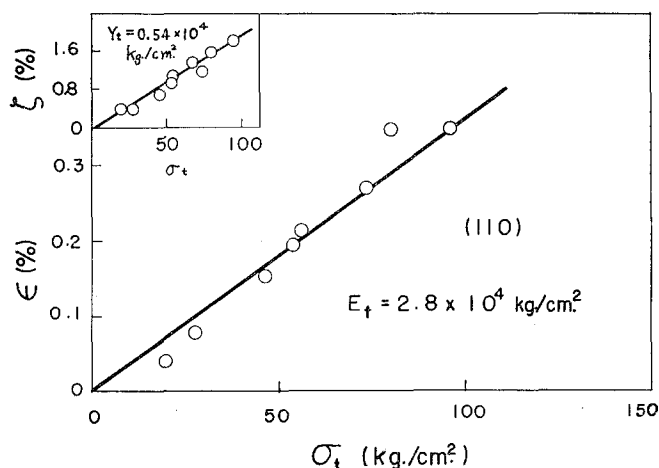


Fig. 15 Stress-strain curves for the lattice and the specimen of low density PE (Sumikathene F101-1; M.I. 0.3).

are listed in Table 9. Fig. 17 shows the E_t -spacing plot for the (110) plane used in the measurements. In this figure, the values obtained by Kobayashi and Nagasawa¹⁰⁾ are also given for electron-irradiated samples of polyethylene. This figure indicates that elastic moduli of crystalline regions decrease with increasing spac-

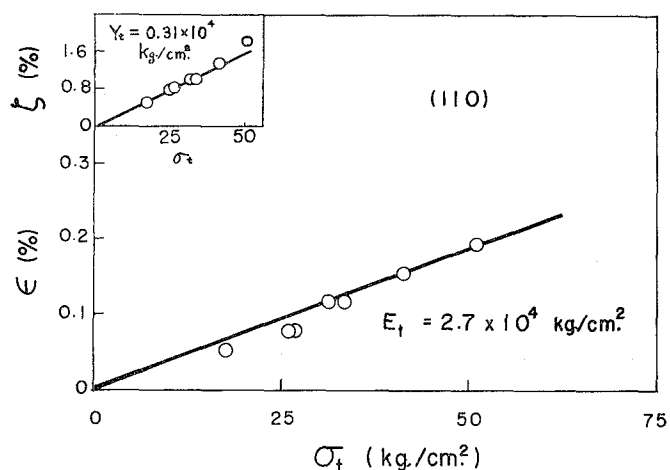


Fig. 16 Stress-strain curves for the lattice and the specimen of low density PE (Sumikathene G806; M.I. 50).

Table 9. Elastic Moduli of Various PE Samples (Unirradiated : $25 \pm 2^\circ\text{C}$, irradiated : $20 \pm 1^\circ\text{C}$.)

Sample	Lattice modulus $E_t(110) (\times 10^4 \text{ kg./cm.}^2)$	Specimen modulus $Y_t (\times 10^4 \text{ kg./cm.}^2)$
Unirradiated		
Scholex 6050	5.3	2.4
Hizex 5000*	4.3	2.0
Sumikathene F101-1 (M.I. 0.3)	2.8	0.54
Sumikathene G806 (M.I. 50)	2.7	0.31
γ -Ray irradiated		
Scholex 6050	4.6	2.1
Sumikathene F101-1	3.2	0.55
Sumikathene G806	2.3	0.36

*) Reported previously

ings, and that the amount of this change is sufficiently large compared to the experimental error ($\pm 10\%$).

As described in the introduction, it was assumed that the stress was homogeneous throughout the length and breadth of specimen. In the case of PVA the maximum change of E_t -values observed are less than 20% as was shown in Fig. 9. In addition, this small change does not correspond to the change of orientation shown in Fig. 6, but does closely to the small change of spacing in Fig. 11. These results lead us to a conclusion that the E_t -value is constant regardless of the large change of orientation of crystallites. On the other hand, if the assumption above mentioned is not correct, the stress on the crystalline regions should depend on the degree of crystallinity of specimens when the degree of orientation is held constant. Experimental results, however, show that E_t -value increases only by about 20% as the degree of crystallinity increases by a factor of 2. Moreover, considering

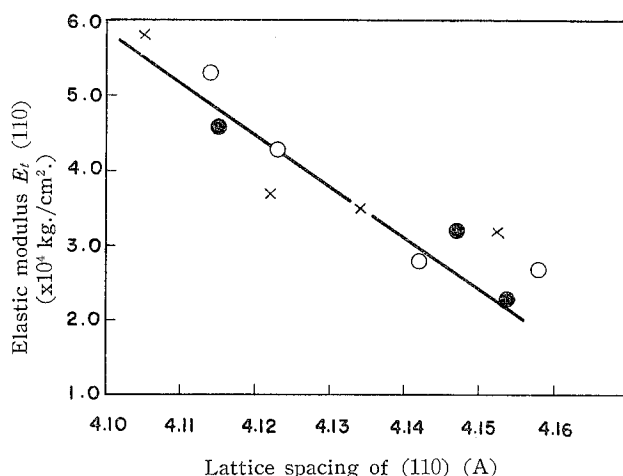


Fig. 17 Relation between lattice spacing and elastic modulus for (110) of PE.

○ unirradiated, ● γ -ray irradiated, × electron irradiated (by Kobayashi *et al.*)

the relation between spacings and E_t -values shown in Fig. 13. E_t -value can be regarded to be independent of the degree of crystallinity. The two experimental facts above described indicate that the above assumption concerning the homogeneous stress is correct.

The maximum E_t -values for PVA and PE observed by us are as follows:

PVA (10 $\bar{1}$) : $E_t = (11 \pm 1) \times 10^4$ kg./cm.² at 20°C

PE (110) : $E_t = (5.3 \pm 0.5) \times 10^4$ kg./cm.² at 25°C

In order to obtain the E_t -value of the perfect crystal from the relation between lattice spacings and elastic moduli, the lattice spacing of the perfect crystal is required.

Walter and Reding¹¹⁾ have reported that the unit-cell dimensions for the un-oriented linear polyethylene having virtually no branches are $a=7.36$ Å and $b=4.92$ Å at 25°C. The spacing of the (110) plane calculated from these dimensions is $d_{110}=4.090$ Å. The E_t -value of the (110) plane for this spacing is $(6.5 \pm 0.5) \times 10^4$ kg./cm.² from Fig. 17. Recently Odajima and Maeda¹²⁾ have reported $(6.87 \sim 7.05) \times 10^4$ kg./cm.² at 20°C as a theoretical E_t -value of the (110) plane. This value is nearly equal to that obtained above.

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